

BASELINE CONTAMINANTS STATUS  
and  
PROPOSED MANAGEMENT CRITERIA  
for

SEQUOYAH AND LITTLE RIVER  
NATIONAL WILDLIFE REFUGES  
OKLAHOMA

Study Identifiers  
**2N9 & 2NO4**

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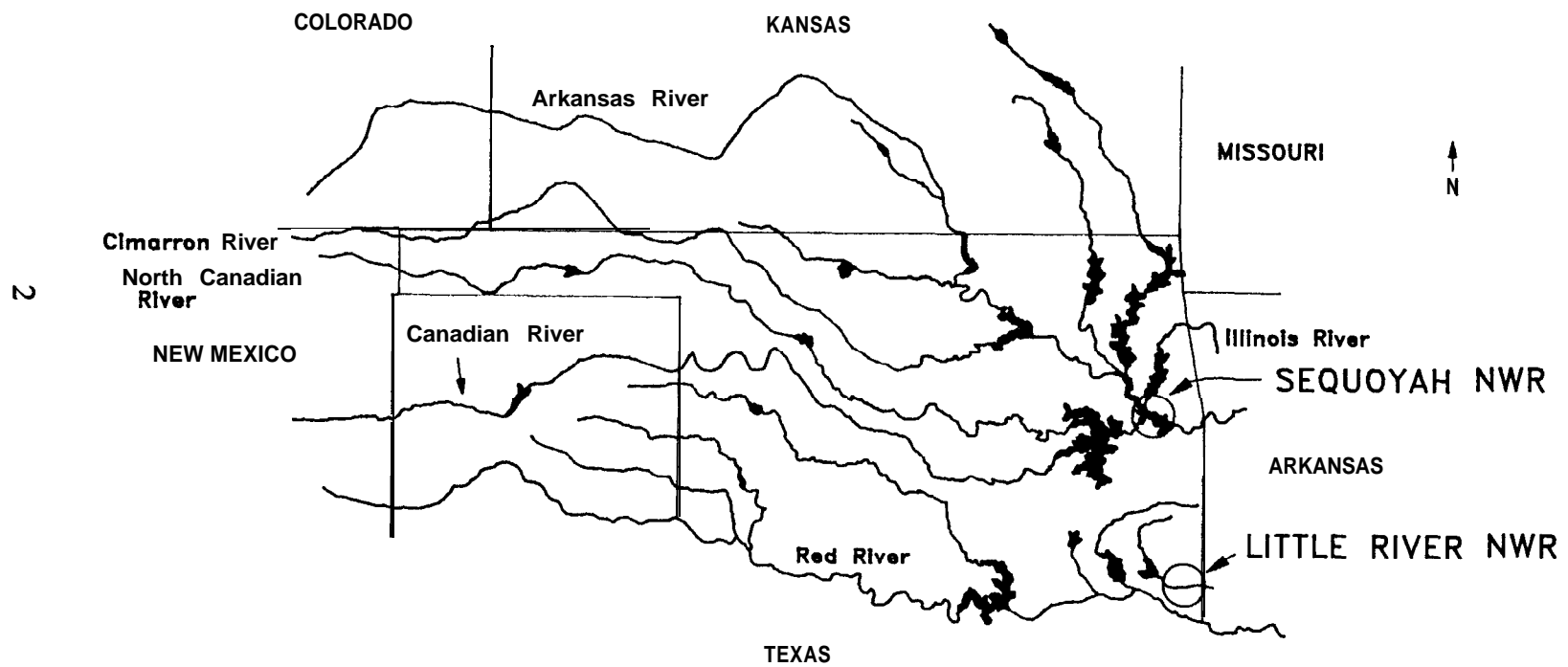


Figure 1. Location of Sequoyah and Little River National Wildlife Refuges in Oklahoma.

Little River NWR (Little River) is a relatively narrow strip of wetlands and bottomland hardwoods located along the lower Little River in Oklahoma (Figures 1 and 3). Tributaries include the Little River upstream **from** the refuge, the Glover and Mountain Fork Rivers, and several smaller streams (Figure 3).

In contrast to Sequoyah, the drainage basin above Little River is relatively small (11,000 sq. km.) and homogeneous, and has a lower population density. Over 80 % of the watershed is forested, with grassland comprising an additional 15 %. Cultivated **cropland** is scarce, but there is a large and rapidly expanding confined poultry and swine feeding industry located throughout the basin. Other industrial activity is primarily associated with the treatment of lumber and the manufacture of forestry-related products such as plywood and fiberboard. Most of the Little River watershed is located in the Ouachita Mountains ecoregion, with limited portions (to the west and south) connected to the South Central Plains and Central Oklahoma/Texas Plains ecoregions (Omernik 1987).

## METHODS

All samples were collected during the summer (May-September), from 1980 through 1991 (Table 1), by FWS personnel from the Oklahoma Ecological Services Field Office. Samples collected during a given summer were analyzed that same year by FWS contract laboratories. Throughout the study, the standardized methods of sample collection, handling, and chemical analysis described in the following sections were used in an effort to obtain a uniform **dataset**. It is easily recognized that in a multi-year study, changes in field personnel and analytical laboratories, may result in data inconsistencies. However, unless otherwise noted, all available data are included in this report and are considered comparable.

### Sample Collection

Thirty-four sediment samples were taken from 15 locations at Sequoyah (Table 2). The habitats sampled included the main river channels (5), backwater areas along the three main rivers (4), depositional areas at the mouths of seven small tributaries (17), and Sally Jones Lake, a large, shallow oxbow (7). One sample was taken from the mouth of a drainage ditch, which at the time served as the NPDES outlet from Sequoyah Fuels, Inc., a uranium processing plant.

Thirty-two sediment samples were taken from nine locations at Little River (Table 2). These included four from the upper Little River (above Pine Creek Reservoir), five from the lower Little River (below the mouth of the Mountain Fork River), eight from the middle Little River (between Pine Creek Dam and the mouth of the Mountain Fork River), four from

Table 1. Sample collection schedule at Sequoyah and Little River National Wildlife Refuges.  
Samples were collected between May and September in each year.

	Year								Total
	1980	1984	1985	1986	1987	1989	1990	1991	
Sequoyah									
Sediment	--	--	6	9	6	--	8	5	34
Fish	2	--	15	19	27	--	--	--	63
Birds	--	--	--	15	—		—	—	15
Little River									
Sediment	--	18	--	--	--	6	8	--	32
Fish	--	16	—	--	--	26	—	—	42
Birds	--	--	28	--	--	--	—	—	28

the Mountain Fork River (above Broken Bow Reservoir), seven from the Glover River, and one each from the lower reaches of Yashau, **Lukfata**, Holly and Mud Creeks.

In shallow water, sediment samples were collected by hand using a stainless steel spoon. In deeper water, a stainless steel Ponar or Ekman dredge was used to collect sediment. In either case, the upper 5 cm of undisturbed substrate was scooped directly into chemically precleaned, widemouth glass jars. Once the jars were filled, they were sealed with aluminum foil, stored on ice in the field, and later refrigerated until ready for analysis.

Sixty-three fish samples, consisting of eleven species, were collected from ten locations at Sequoyah, which is a typical warmwater, reservoir fishery (Tables 2 and 3). Fish were collected from all main habitat types and at most of the same locations where sediment samples were taken. Three small tributary embayments (Little Vian Creek, Snakerock Creek, and Dirty Creek), the Sequoyah Fuels discharge, and the Canadian River backwaters were not sampled for fish.

Forty-two fish samples, consisting of eleven species, were collected from five locations at Little River, which can be described as a coolwater, stream fishery (Table 2 and 3). Fish were taken in the same vicinity as sediment: Upper Little River (9); middle Little River (10); lower Little River (6); Glover River (10); and, Mountain Fork River (7). Fish were not collected from the small tributary streams.

Fish were collected with gill nets, seines, trap nets, and electrofishing equipment. Individual fish were immediately identified, weighed and measured. Composite samples (usually consisting of five, similarly-sized fish) of the same species were wrapped with aluminum foil and placed on ice in the field. The composite samples were frozen as quickly as possible, and remained so until submitted for chemical analysis. Common and scientific names of fish (Table 3) follow the Committee on Names of Fishes, American Fisheries Society (1991).

Fifteen bird tissue samples were collected at Sequoyah in 1987. Five pre-fledgling, double-crested cormorants (**Phalacrocorax auritus**), were collected from nests located in the Negro Creek embayment. Eight young tree swallows (**Tachycineta bicolor**) were taken from nests in the vicinity of Sally Jones Lake. One dead interior least tern chick (**Sterna antillarum**) was salvaged from a sand bar near the mouth of the Canadian River. All birds were immediately skinned, and the beaks, feet and GI tracts removed. Four composite samples of tree swallows (consisting of two birds each) and the interior least tern were submitted for whole-body analyses of selected elements and organochlorine compounds. Cormorant livers were submitted individually for element analyses. The five cormorant carcasses (minus the livers) were submitted individually for element and organochlorine analyses. Birds were kept on ice in the field and later **frozen** until ready for analysis.

Twenty-eight wild turkey (Meleagris gallopavo) livers were obtained from birds taken by hunters in the Little River Basin in 1985. Ten were taken from birds killed in the upper Little River Basin (above Pine Creek Dam), ten were from the upper Mountain Fork River Basin (above Broken Bow Dam), and eight were from the Glover River Basin. Hunters were provided with instructions for removal and handling of the liver, prior to the hunt. Livers were removed in the field, placed in plastic bags, sealed, and returned to the hunter check station along with a map showing the location of the kill. Livers were frozen and later submitted individually for organochlorine analyses.

### Sample Analysis

All samples were submitted for analysis to FWS contract laboratories through the Patuxent Analytical Control Facility (PACF). A rigorous program of methods standardization and quality assurance/quality control (QA/QC) assessment was maintained by PACF for all contract laboratories. Procedural blanks, duplicates, spiked samples, and analysis of standard reference materials were used routinely with each batch of samples to evaluate and maintain QA/QC.

An organochlorine (OC) scan was performed on all sediment, fish, whole-body bird, and wild turkey liver samples. An OC scan included quantification of the following compounds: **p,p'**-DDE, **p,p'**-DDD, **p,p'**-DDT, **o,p'**-DDE, **o,p'**-DDD, **o,p'**-DDT, HCB, alpha BHC, gamma BHC, dieldrin, heptachlor epoxide, oxychlordane, cis-chlordane, trans-chlordane, cis-nonachlor, endrin, endosulfan, trans-nonachlor, methoxychlor, DCPA (**Dacthal**), mirex, toxaphene, and PCB-Total (PCB). The lower limit of detection for toxaphene and PCB in sediment and animal tissue was 0.05 **mg/kg wet-weight**. For all other compounds, the detection limit was 0.01 **mg/kg wet-weight**. Each OC scan in animal tissue included the quantification of percent lipid and moisture. Percent moisture was determined for sediment. Methods of sample preparation and residue analysis have been described by Cromartie et al. (1975), Kaiser et al. (1980) and Schmitt et al. (1985). Following homogenization, extraction, clean-up and separation, the resulting fractions were analyzed by electron-capture gas chromatography. Residues in 10% of the samples were confirmed by gas chromatography/mass spectrometry. All results of OC analyses in sediment and animal tissue are expressed on a dry weight basis.

Options for purchasing element analyses from contract laboratories changed between 1980 and 1991. State-of-the-art techniques for analyzing individual elements in sediments and animal tissue improved throughout the course of this study. The same elements were not always selected for each batch of samples, either because of availability or cost constraints. In this report, only those element data that resulted from comparable methods of sample digestion and analysis have been included. The foregoing factors have resulted in a **final dataset** with differing numbers of samples for the various elements in each matrix. Aluminum, cadmium, chromium, copper, iron, lead, magnesium, manganese, nickel and zinc have been determined by inductively coupled plasma(ICP) emission spectroscopy or graphite furnace atomic absorption (GFAA); mercury was determined by cold vapor atomic absorption (CVAA); and, arsenic and selenium were determined by either hydride generation (HGAA) or GFAA. Digestions preceding the ICP, GFAA, and HGAA determinations utilized either a mixture of hydrochloric and nitric acids or a mixture of nitric and perchloric acids.

## RESULTS AND DISCUSSION

### ORGANOCHLORINES

#### Sediment

No OC residues were detected in any of the 32 sediment samples collected from Little River. One OC, **p,p'-DDE**, was detected in 4 1% (14/34) of the sediment samples collected from Sequoyah, at concentrations ranging from 0.01 to 0.16 **mg/kg**. There appeared to be a decrease in both frequency of detection and concentration of DDE in sediments at Sequoyah during the course of the study. From 1985 to 1987, DDE was found in 57% (12/21) of the samples collected, while in 1990 and 1991, only 15% (2/13) of the samples had detectable concentrations. The three highest concentrations of DDE encountered in Sequoyah sediment (0.16, 0.09, and 0.04 **mg/kg**) occurred in 1985. After 1985, detectable concentrations ranged between 0.01 and 0.03 **mg/kg**.

Five other OC compounds (**p,p'**-DDD, gamma BHC, oxychlordane, **heptachlor** epoxide, and **trans-nonachlor**) were found in one sediment sample from Sequoyah, at concentrations near the lower limit of detection (0.01 **mg/kg**). This sample was collected in 1986 from the Illinois River channel, directly downstream from the Sequoyah Fuels, Inc. NPDES discharge site.

It is not possible to conclusively evaluate the status of OC contamination at either Little River or Sequoyah based solely on the available sediment data. If one considers the “Lowest Effect Level” concentrations listed for various OC compounds by **Persaud** et al. (1993) or the “Effects Range-Low” concentrations for the same OCs given by Long and Morgan (1990), one finds that the values for most OCs in either list are lower than the limits of detection that were used for OCs in this study. In other words, these particular sediment quality guidelines imply that adverse effects to some benthic organisms are possible, perhaps even probable, at concentrations below those which we were able to detect and/or quantify.

All DDE concentrations detected in Sequoyah sediment approached or exceeded Long and Morgan's (1990) “Effects Range-Median” value of 0.015 **mg/kg**, although these authors state that their degree of confidence in this specific value is relatively low. It is not possible to compare **Persaud** et al. (1993) “Severe Effect Level” for DDE directly to the Sequoyah data, since their values are normalized to organic carbon. Nevertheless, by using a range of organic carbon values that are likely to occur in Sequoyah sediment, it is not likely that normalized DDE values, estimated from data in this study, would exceed “Severe Effect Levels”. Thus, the use of these two different references as guidelines results in a somewhat ambiguous conclusion with regard to predicted effects of detected levels of DDE in Sequoyah sediment on benthic organisms.

Aside from the direct effects that OC compounds in sediment may have on benthic organisms, one can also consider the sediment as a potential source of OCs that can bioaccumulate in members of the aquatic food chain (Willford et al. 1987; Bishop et al. 1995). Bioaccumulation



One or more isomers of DDT were detected in all 63 samples of fish collected from Sequoyah (Table 4). DDE was universal, occurring at concentrations ranging from 0.11 to 9.4 mg/kg. DDD was detected in 92% of the samples at concentrations up to 1.2 mg/kg. The parent compound DDT, was present in 52% of the total samples taken with a maximum concentration of 0.33 mg/kg. The geometric mean for total DDT (sum of DDE, DDD, and DDT) was 1.4 mg/kg, with a range of 0.11 to 9.8 mg/kg. Over two-thirds (70%) of the samples exceeded 1.0 mg/kg total DDT. There were significant differences in geometric mean concentrations of total DDT among the three primary years of collection, with 1985 being highest (2.1 mg/kg) and 1986 the lowest (0.94 mg/kg). The same laboratory was used for analysis in both years, thus it seems probable that location and/or species differences among years may have been responsible for the annual variations observed.

Because sites, major habitat types, and individual species were not sampled with comparable effort during each of the years studied, it is not practical to statistically test location or species differences in concentrations of DDT isomers at Sequoyah. Two species, striped bass and white bass, appeared consistently high in total DDT. All samples of the former exceeded 2.0 mg/kg, while all those of the latter exceeded 3.0 mg/kg. All samples of white bass were collected in 1985 from three different habitat types, while all striped bass were collected in 1987 at three separate locations. One species appeared to be consistently low in total DDT. All samples of gizzard shad, which were collected in 1986 from four different habitat types, contained less than 0.7 mg/kg total DDT. All other species, for which there were four or more samples taken, exceeded 1.0 mg/kg total DDT in 70 to 80 percent of their samples.

Ratios of DDE to total DDT (Table 4) were much less variable than the concentrations of DDT isomers both within and among species. The average DDE/total-DDT ratio for all samples was 0.84, with a coefficient of variation of only 13%. Individual ratios were greater than 0.80 in 75% of the samples, and coefficients of variation within species varied from 3.5 to 15 percent.

Chlordane, heptachlor epoxide, and dieldrin (Table 5) were detected in Sequoyah fish samples at frequencies of 89%, 57%, and 19%, respectively. Geometric means for detectable concentrations were 0.12 mg/kg chlordane, 0.03 mg/kg heptachlor epoxide and 0.05 mg/kg dieldrin. None of the dieldrin concentrations, and only two of heptachlor epoxide, exceeded 0.10 mg/kg, whereas, over half (54%) of the detectable chlordane concentrations were in excess of 0.10 mg/kg.

Table 5. Frequency of occurrence (%) and maximum concentrations (mg/kg dry weight) of chlordane, heptachlor epoxide, and **dieldrin** in whole-body fish and birds collected from Sequoyah National Wildlife Refuge, 1980- 1991. National and regional data for whole-body fish from the National Contaminants Biomonitoring Program (Schmitt et al. 1990) are shown for comparison.

Location /Species	N	Chlordane <sup>1</sup>		Heptachlorepoxyde		Dieldrin	
		Freq	Max	Freq	Max	Freq	Max
Sequoyah							
Common Carp	20	85	0.37	45	0.12	15	0.07
Largemouth Bass	10	100	0.44	40	0.04	10	0.07
Channel Catfish	7	100	0.50	100	0.08	14	0.04
Striped Bass	5	100	0.18	100	0.05	40	0.05
Gizzard Shad	5	60	0.13	0.00	--	20	0.05
White Bass	4	75	1.04	50	0.17	50	0.07
Blue Catfish	4	75	0.80	50	0.07	50	0.04
Smallmouth Buffalo	4	100	0.20	75	0.03	0.00	--
Shiners	2	100	0.06	100	0.04	0.00	--
Bluegill	1	100	0.07	100	0.02	0.00	--
White Crappie	1	100	0.07	100	0.02	0.00	--
Double-crested Cormorant	5	100	0.09	100	0.05	20	0.04
Tree Swallow	4	100	0.10	75	0.07	25	0.03
Interior Least Tern	1	100	0.11	100	0.07	0.00	--
Regional?							
Common Carp	20	70	1.04	10	.08	20	.12
Largemouth Bass	10	80	.24	10	.04	40	.04
National <sup>3</sup>							
47 species	321	89	>4.0	49	1.2	74	5.6

<sup>1</sup> Sum of *cis*-chlordane, *cis*-nonachlor, *trans*-chlordane, *trans*-nonachlor, and oxychlordane

<sup>2</sup> 10 locations on major rivers in Oklahoma (4), Arizona (4), Arkansas (1), and New Mexico (1), chosen because both common carp and largemouth bass were included for the same location in 1984.

<sup>3</sup> 112 locations nationwide in 1984.

totals in the remaining group. The fish from Little River never approached these concentrations of OC pesticides, therefore, all species should be considered safe for consumption by avian wildlife. On the other hand, a few species of fish **from** Sequoyah did exceed the advisory levels for both DDT and other **Oct** (Tables 4 and 5). Maximum concentrations of total DDT found in largemouth bass, white bass and blue **catfish**, as well as the mean concentration in white bass, did exceed the NA/NA guidelines. Also, some samples of largemouth bass, white bass, blue catfish and channel catfish exceeded the guidelines for other Oct. These findings suggest that at Sequoyah, some individual fish of certain species may contain enough **Oct** to adversely effect fish-eating birds. It should be noted that the mean concentrations for **OCs** in all species of fish at Sequoyah are only about one-quarter of the NA/NA guidelines.

Schmitt et al. (1990) reported the results of the 1984 National Contaminants Biomonitoring Program (NCBP), in which 32 1 fish samples were analyzed for **OCs** from 112 stations nationwide. The wet weight values given in their paper were converted to dry weights using an assumed average of 75% moisture. The geometric mean concentration of total DDT in fish from Sequoyah (1.4 **mg/kg**) exceeded that found in fish nationwide (Table 4). A similar comparison of maximum values of DDT is not relevant, since the national maximum is from a well known, highly contaminated site. Nationally, the frequency of occurrence for DDE and DDD is similar to Sequoyah, however, DDT appears to be more prevalent nationwide. Chlordane and heptachlor epoxide were found with about the same average frequencies and with similar mean concentrations in Sequoyah as were found in the national survey (Table 5). However, **dieldrin** appeared less frequently and at a markedly lower mean concentration at Sequoyah.

Data from Schmitt et al. (1990) were also used to make a regional comparison involving common carp and largemouth bass (Tables 4 and 5). Ten locations, on major rivers in Oklahoma, Arizona, Arkansas and New Mexico, were chosen from the national **dataset** because they included simultaneous collections of both species. Mean concentrations of total DDT for both species in the regional **dataset** were markedly less than Sequoyah, and except for DDE, the frequencies for specific isomers were also higher at Sequoyah. Differences between the regional **dataset** and Sequoyah for chlordane, heptachlor epoxide and dieldrin are less distinct.

Ratios of DDE to total DDT are often useful in explaining certain aspects of DDT contamination at specific localities (Aguillar 1984, Schmitt et al. 1990, Winger et al. 1990). In general, it is assumed that lower ratios (less than 1 .O) imply an unweathered (or recently applied) source of the parent compound, DDT. The ratio at Little River was 1 .O (the highest possible score). This suggests that the source of DDT in this watershed is relatively old and/or well weathered. The geometric mean ratio at Sequoyah of 0.84, suggests a less weathered, or more recent source of DDT at this locality. Individual species differ with respect to their DDT metabolism (Schmitt et al.1990), and this factor, coupled with the obvious differences that may exist in bioavailability, probably account for the range of differences seen within and among species in Table 4. Ratios in common carp and largemouth bass at Sequoyah appear comparable to the regional **dataset** previously mentioned, while the mean for combined samples is higher than the national average (Table 4).

Table 6. Organochlorine pesticide concentrations (**mg/kg** dry weight) and frequency of detection (%) in wild turkey livers collected from three areas in the Little River watershed in 1985.

	Upper Little River (n=10)			Glover River (n=8)			Mountain Fork River (n=10)		
	Freq	G.M. <sup>1</sup>	Max	Freq	G.M.	Max	Freq	G.M.	Max
DDE	80	0.04	0.16	100	0.05	0.30	100	0.10	0.26
<b>Chlordane<sup>2</sup></b>	70	0.01	0.03	75	0.02	0.03	90	0.03	0.11
Heptachlor epoxide	70	0.01	0.03	62	0.01	0.07	90	0.02	0.08
Dieldrin	80	0.01	0.03	25	0.01	0.02	90	0.02	0.09

<sup>1</sup>Geometric Mean

<sup>2</sup> Sum of cis-chlordane, cis-nonachlor, *trans*-chlordane, *trans*-nonachlor, and oxychlordane

River due to the fact that liver samples were placed and stored in plastic bags. Plastic may absorb **OC** and therefore reduce concentrations found in the samples. Liver tissue is probably not the best choice for interpreting the significance of OC residues in birds, either individually or at the population level. If one wants to consider the potential for lethality, brain tissue is probably the best choice; and, if one is interested in reproductive effects, eggs are probably the best selection (Stickel et al. 1984). Nevertheless, the liver data from this study indicate that wild turkeys in the headwaters areas of the Little River Basin appear to be in no danger of being adversely effected by OC compounds.

Whole-body concentrations of OC compounds in cormorants from Sequoyah were substantially less than those reported by Ohlendorf et al. (1991) for surfscoters in San Francisco Bay or by Mora and Anderson (1991) for cormorants in agricultural areas of northwestern Mexico. In the former study, DDE concentrations reached as high as 12 **mg/kg** and dieldrin 1.6 **mg/kg**; and the authors concluded that survival or reproduction in these birds would not be affected. In the latter study, maximum DDE concentrations approached 50-60 **mg/kg**, with no apparent adverse effects. The Sequoyah data is probably biased in relation to the above cited studies due to the fact that birds from Sequoyah were skinned while those from the comparative studies were plucked. Much of the carcass OC residue is located in the subcutaneous fat, resulting in lower estimates from Sequoyah. Based on the only available data, it appears that neither cormorants nor tree swallows from the Sequoyah area are likely to experience reproductive problems from DDE or other OC compounds.

## ELEMENTS

### Sediment

Ten elements (aluminum, arsenic, chromium, copper, iron, lead, magnesium, manganese, nickel and zinc) were always present at detectable concentrations in sediment samples from Little River and Sequoyah (Table 8). The range in concentration for each of these elements spanned an order of magnitude at each location. Coefficients of variation ranged from 65% (zinc) to 108% (lead) at Little River, and between 41% (arsenic) and 78% (manganese) at Sequoyah. Given this much variation in the data, measurements of central tendencies are somewhat weak, and spatial differences within the two locations are hidden. Overall however, mean concentrations for arsenic, magnesium, nickel and zinc were significantly higher at Sequoyah than at Little River.

At Little River, cadmium, mercury and selenium were not consistently found in sediment at concentrations above their stated detection limits (0.20, 0.02, and 0.20 **mg/kg**, respectively). The same was true for cadmium and selenium in Sequoyah. However, mercury occurred at concentrations slightly above the detection limit in all samples from Sequoyah. These limited data suggest that mercury and selenium were not as variable

as the more common elements at either Sequoyah or Little River. Cadmium appeared variable, especially at Little River.

Bulk element concentrations in sediment from the same watershed are **often** related to the texture of the sample, due to (1) the chemical similarity of geologic parent material within the watershed, and (2), the affinity of individual elements for the finest grain-size fractions (de Groot, 1995). Therefore, correlation coefficients between the concentration of each element and the percent composition of each grain-size fraction (sand, silt, clay) were calculated for Sequoyah and Little River. The highest correlation for each element at both locations was always obtained in relation to the clay fraction. Not all of the correlations at each location were significant, but when data from both locations were combined, every element was significantly correlated with the clay fraction (Table 9).

Significant correlations, and their corresponding linear regression lines (Table 9), can be used in several ways. First, the concentration of an element in a whole group of co-genetic sediments can be expressed by a single value, which is obtained by extrapolating the regression line for that element to 100% clay (de Groot, 1995). This application could be used here to compare Little River and Sequoyah with respect to some of the more highly correlated elements such as copper. It is limited however, by the lack of significant correlations for all elements at both locations, and by the somewhat small sample size.

The significant correlations for combined locations (Table 9) were used as rationale for calculating clay-normalized concentrations for each element in each sample (Hebert and Keenleyside 1995). Normalization of the data greatly reduced the magnitude of the range and the coefficient of variation for nearly every element at both locations (Table 10). This overall reduction in variation should make measurements of central tendencies more meaningful, and statistical comparisons between the two locations more robust. No statistically significant differences were found between clay-normalized concentrations of elements in Sequoyah and Little River sediments (Table 10). These data suggest that both locations are part of one co-genetic sediment group with respect to element content. Therefore, variation in bulk element concentrations within or between locations is expected to be in large part due to textural properties of the individual sediment samples.

In order to evaluate the status of element contamination in sediment from Sequoyah and Little River, comparisons were made between the bulk concentrations summarized in Table 8 and the guidelines of Long and Morgan (1990) and Persaud et al. (1993) shown in Table 11. Seven elements (arsenic, cadmium, chromium, copper, iron, manganese and nickel) exceeded the latter authors' "Lowest Effect" concentration at least once at both locations. In addition, there was one exceedence for lead at Little River and two for zinc at Sequoyah. Mercury was the only element that did not exceed any of the guidelines in Table 11 at either location. Lemly and Smith (1987) suggested 4 **mg/kg** as the level of

Table 10. Summary of clay normalized element concentrations (mg/kg dry weight) in sediment from Sequoyah and Little River National Wildlife Refuges, 1980- 1991.

	Sequoyah (n= 13)		Little River (n=8)		Combined (n=21)	
	Mean	C.V. <sup>1</sup>	Mean	C.V.	Mean	C.V.
	Range		Range		Range	
Aluminum	93,000	27%	110,000	34%	100,000	32%
	50,000-130,000		81,000-210,000		50,000-210,000	
Arsenic	40	39%	27	30%	35	41%
	19-82		19-44		19-82	
Chromium	140	34%	160	41%	150	37%
	60-240		88-290		60-290	
Copper	66	25%	61	34%	64	28%
	47-110		40-100		40-110	
Iron	140,000	35%	120,000	39%	130,000	36%
	67,000-220,000		75,000-200,000		67,000-220,000	
Lead	130	44%	200	51%	154	53%
	63-240		100-350		63-350	
Magnesium	14,000	45%	9,400	40%	12,000	49%
	7,100-32,000		6,000-18,000		6,000-32,000	
Manganese	3,600	50%	6,200	88%	4,700	81%
	1,800-8,700		1,500-17,000		1,500-17,000	
Mercury	0.36	40%	--	--	--	
	0.23-0.80					
Nickel	120	31%	96	45%	110	37%
	63-210		67-200		63-210	
zinc	340	20%	300	35%	320	26%
	250-510		190-500		190-510	

<sup>1</sup>C.V. = Coefficient of Variation: (Standard Deviation / Mean) x 100

\* Statistically significant difference between mean concentrations at Sequoyah and Little River (P<0.05)

concern for selenium in sediments. Neither Little River nor Sequoyah approached this concentration. No guidelines were found for aluminum or magnesium.

Table 11 shows a fairly wide divergence between the “Lowest Effect” concentration of Persaud et al. (1993) and the “ER-L” concentration of Long and Morgan (1990). If the latter authors’ concentrations are considered alone, then exceedence is reduced to only one element (lead) at Little River and two elements (nickel and zinc) at Sequoyah. Background concentrations are also important in evaluating the degree of element contamination at any specific location. Persaud et al. (1993) note that background may indeed exceed their “Lowest Effect” concentrations, in which case, the former must be considered the management objective for sediment quality.

The best evaluation that can be made on the basis of the present data is that sediment at Sequoyah and Little River is not seriously contaminated with any of the elements analyzed. Two questions remain to be answered: (1) Which of the two sets of guidelines (i.e. “Lowest Effect” or “ER-L”) are adequately protective for benthic organisms at Sequoyah and Little River; and (2) What are the true background concentrations for elements at the two locations in question.

### **Fish**

Seven elements (aluminum, arsenic, chromium, copper, iron, manganese, and zinc) were always present at detectable concentrations in fish samples from Little River and Sequoyah (Table 12). Two additional elements (nickel and selenium) were present at detectable concentrations in all samples from Sequoyah, but were not sampled at Little River. One element (magnesium) which was always present at Little River, was not analyzed in samples from Sequoyah. Cadmium was detected in 100 percent of the samples from Little River, and in over two-thirds (72%) of the samples from Sequoyah. Concentrations of lead above the detection limit (0.50 ppm) were found in only about one-quarter of the samples analyzed at both locations. Mercury was not analyzed in any of the fish samples from either location.

The range in concentration for each element detected at Sequoyah spanned an order of magnitude. Coefficients of variation ranged from 25% (selenium) to 128% (iron). At Little River, a similar wide range in concentrations was noted for all elements detected except chromium and zinc. Coefficients of variation ranged from lows of 18% (zinc) and 24% (chromium) to a high of 174% (aluminum). For the most part, apparent spatial differences in the element composition of fish, either between or within these two locations, were masked by the variation in the data. As was found with respect to the bulk sediment data, some mechanism for reducing this variation was necessary in order to compare element concentrations in fish at Sequoyah and Little River.



Different species of fish, taken **from** the same location, often contain different concentrations of a particular element due to differences in (1) physiology, (2) foraging strategies, or (3) exposure conditions (Wiener and Giesy, 1979; Lowe et al., 1985; Campbell, 1994). With this in mind, an attempt was made to determine which fish species at Sequoyah contained the highest and lowest concentration of each element (Table 13). Only species with five or more samples for a given element were included, and differences were tested using both parametric and non-parametric procedures. Common carp contained the highest mean concentration of eight elements - aluminum, cadmium, chromium, lead, manganese, nickel, selenium and zinc. Gizzard shad had the highest mean concentration of the other three elements - arsenic, copper and iron. Largemouth bass had the lowest mean concentration for five elements - cadmium, iron, lead, nickel, and zinc. Channel catfish was lowest for copper and selenium, while common carp contained the lowest arsenic. Specific lows for aluminum, chromium, and manganese were not calculated because of insufficient data.

The difference in concentration between the highest and lowest species was statistically significant for six of the eleven elements (Table 13). Three of the remaining five cases could not be tested because of insufficient data. In one non-significant case (nickel) the **intraspecific** variation remained very high, while in the other (selenium), **interspecific** differences were low. In every case except nickel and selenium, the coefficient of variation for both the high and low species was markedly less than those for combined species.

It is apparent that comparisons of element concentrations in fish, between and/or within locations, should utilize data from the same species. Because of the manner in which the species data were distributed in this study, it was not practical to statistically compare Sequoyah and Little River. However, certain trends can be gleaned from the data. For example, at Little River, the mean concentration of arsenic in gizzard shad (1.0 **mg/kg**) was nearly four times higher than the mean for all other species combined (0.28 **mg/kg**). Also, the highest concentrations of arsenic encountered at Little River were found in gizzard shad. These observations would support the conclusion drawn from the Sequoyah data, that gizzard shad are consistently higher in arsenic than other species in this study. The fact that mean gizzard shad values for arsenic at Little River and Sequoyah appear comparable, suggests that there is probably no real difference in the concentration of this element in fish at the two locations. Gizzard shad can also be used to compare copper concentrations in Sequoyah and Little River. In the latter, gizzard shad averaged 4.0 **mg/kg** (C.V.=20%). This value was significantly lower than the average for the same species in Sequoyah, suggesting that there may be a difference in concentrations of copper in fish at the two locations.

Many elements are essential for biochemical reactions in fish, and are thus always present in trace amounts. Others are non-essential, but may also be present at detectable concentrations. Interspecific differences, such as those discussed in the present study,

complicate efforts to standardize guidelines or criteria for element concentrations. In order to evaluate the status of element contamination in fish **from** Sequoyah and Little River, generalized comparisons were made to the concentrations reported from other studies and to recommendations for specific elements found in the literature.

Aluminum is abundant in aquatic sediment, and in most situations is not toxic. Acidification of aquatic environments brings aluminum into solution and increases toxicity. Concentrations of aluminum in whole-body fish samples of the same species are often highly variable, and may reflect the presence of aluminum-bearing sediment in the gut (Winger et al. 1990). The significance of aluminum concentrations in fish is largely unknown, but the concentrations in Sequoyah and Little River are assumed to represent background conditions.

Arsenic does not normally **biomagnify** in fish (Winger et al. 1990), and it has been observed that accumulations of this element are generally higher in planktivorous fishes than in predators and omnivores (Hunter et al. 1981). The mean concentration of arsenic in combined fish samples from Little River was less than the mean from the National Contaminants Biomonitoring Program (NCBP) shown in Table 14. The mean in combined fish samples from Sequoyah was slightly higher than the national mean, but substantially less than the 85th percentile. When means for common carp and largemouth bass **from** Sequoyah were compared to the means for same species in the Regional **dataset** (Table 14), the latter were slightly higher in both cases. Arsenic is not considered to be a contaminant problem at Sequoyah or Little River.

Cadmium is **highly** toxic to fish, and may be present in a variety of industrial and municipal wastes. The mean concentration of this element in all fish samples from Little River was less than the NCBP mean (Table 14). In Sequoyah, the combined mean (for those samples above the detection limit) was equivalent to the NCBP 85th percentile. The mean values for common carp and largemouth bass in Sequoyah and in the Regional **dataset** were very comparable (Table 14). Concentrations of cadmium in fish from contaminated areas (c.f. Winger et al. 1990 and Campbell 1994) are substantially higher than those found in this study. Eisler (1985) suggested 0.40 **mg/kg** as a dietary threshold concentration for cadmium in food-chain organisms. A few individual fish from Sequoyah exceeded this value, however, the incidence was less than 10%. Cadmium contamination is not presently considered a problem in Sequoyah or Little River, but concentrations in fish should be monitored.

Chromium is a contaminant **often** associated with the electroplating industry or with cooling water from electric power generation. It is readily absorbed and rapidly eliminated by fish. Eisler (1986) reported that the significance of chromium residues is unclear, but available evidence suggests that concentrations in excess of 4.0 **mg/kg** dry weight should be viewed as presumptive evidence of chromium contamination. At Little River, chromium concentrations were always less than 4.0 **mg/kg**, while at Sequoyah about 10% of the total

samples exceeded this value. The mean concentration of about 2.0 **mg/kg** at both locations suggests that neither is significantly contaminated.

Copper contamination in aquatic environments may result from urban runoff, sewage treatment plants, leachates from municipal landfills, and a variety of industrial discharges. The mean concentration of copper in fish from Little River was intermediate between the NCBP mean and 85th percentile, while the mean at Sequoyah exceeded the 85th percentile (Table 14). A comparison of mean values in common carp and largemouth bass at Sequoyah (5.6 and 3.8 **mg/kg**, respectively) with those same species in the Regional **dataset**, revealed once again that Sequoyah was slightly higher. When values from Sequoyah are compared to other so-called “background” concentrations from other areas (Winger et al. 1990 or Campbell 1994), they are notably less. The National Research Council (1980) recommends 1,200 **mg/kg** copper as the dietary threshold concentration for food-chain organisms. Copper concentrations may be somewhat elevated in fish from Sequoyah, but they would not appear to constitute a serious biological problem.

Iron is an essential element for plants and animals and is not generally associated with toxicity or adverse effects on fish or fish-eating predators. Some authors (e.g. Winger et al. 1990) have ascribed the wide variation found in field studies to different amounts of sediment in the gut contents. The data in this study however, support the conclusion that variation within a species is relatively low, and that wide variations are observed among different species. From the limited data in other studies, one can conclude that iron concentrations in fish from Little River and Sequoyah are consistent with background conditions.

Lead is used extensively in today’s society and may occur at elevated concentrations in aquatic environments from a variety of sources. Of particular relevance to Sequoyah, is the presence of an extensive, historic lead and zinc mining area in the Neosho River drainage basin. Campbell (1994) reported lead concentrations of about 50 **mg/kg** dry weight in largemouth bass from “contaminated” stormwater ponds, while the same species from “control” ponds contained about 25 **mg/kg**. Redear sunfish from the same sites contained 63 and 28 **mg/kg** lead, respectively (wet weight values were converted to dry weight assuming 75% moisture). The NCBP mean for lead was 0.44 **mg/kg**. Three-quarters of the samples from both Little River and Sequoyah contained less than 0.50 **mg/kg**. The National Research Council (1980) recommended 200 **mg/kg** lead as the dietary threshold concentration for food-chain organisms. Common carp, gizzard shad, smallmouth buffalo and channel catfish, the only species from Sequoyah to contain detectable concentrations of lead, all averaged well under 1.0 **mg/kg**. Fish are not contaminated with lead at Little River or Sequoyah.

Magnesium is an essential element for certain metabolic processes, and is obviously present in fish at relatively high concentrations. The significance of whole-body concentrations and/or the consequences of potential magnesium contamination in the aquatic environment are unknown.

Manganese was the only element that appeared to be significantly higher in Little River than in Sequoyah (Table 12). In the Savannah River system, manganese in different species of fish varied

The whole-body fish data from this study yielded no clear evidence of element contaminant problems at Sequoyah or Little River. Concentrations of individual elements at both locations ranged in the vicinity of values shown by other authors to be normal or below suggested dietary threshold concentrations for food-chain organisms. These findings are consistent with the earlier evaluation of no serious contamination that was based on element concentrations in sediment.

## **Birds**

Bird tissues from Sequoyah were analyzed for eight elements (Table 15). Concentrations of elements in whole-body cormorants were compared to corresponding liver concentrations and to whole-body swallows using Wilcoxon's two sample test as extended by Mann and Whitney for unequal-sized samples. This test is particularly useful when comparing small sized samples in which one or more of the values for the element of concern is below the limit of detection. Whole-body cormorants had significantly higher concentrations of zinc, lead, and nickel and lower concentrations of copper, iron and selenium, than cormorant livers. Both arsenic and cadmium were below detection in both types of cormorant samples. Whole-body swallows were higher in cadmium, copper, iron and selenium and lower in lead and zinc than whole-body cormorants. There was no difference in arsenic or nickel.

Mora and Anderson (1995) reported 17 **mg/kg** selenium, 81 **mg/kg** zinc, 2.3 **mg/kg** cadmium and 17 **mg/kg** copper in the livers of double-crested cormorants from the Mexicali Valley in Baja, California, and concluded that these values were below biological effects thresholds. Canvasbacks (*Aythya valisineria*) wintering on San Francisco Bay in 1988 had mean liver concentrations of 0.25 **mg/kg** arsenic, 0.56 **mg/kg** cadmium, 99 **mg/kg** copper, 618 **mg/kg** iron, 0.43 **mg/kg** lead, 13 **mg/kg** selenium and 160 **mg/kg** zinc (Miles and Ohlendorf 1993). With the possible exception of selenium, these authors considered concentrations of these potentially toxic elements low. Adult, male surf scoters (*Melanitta perspicillata*) collected from San Francisco Bay in March, 1985 contained liver concentrations of 0.46-1.25 **mg/kg** arsenic, 4.9-9.8 **mg/kg** cadmium, 29-58 **mg/kg** copper, 103-133 **mg/kg** zinc, 781-2070 **mg/kg** iron, 0.18-0.97 **mg/kg** lead and 0.09-1.1 **mg/kg** nickel (Ohlendorf et al. 1991). These authors considered these concentrations of arsenic,

copper, lead, iron, nickel, and **zinc** as non-hazardous. Cadmium was thought to be of “potential toxicological significance” if birds experienced food shortage. Selenium, which averaged about 60 **mg/kg**, was said to be of “potential significance”. Lemly (1993) considered liver concentrations of 10 **mg/kg** selenium as the effects threshold for aquatic birds.

The comparison of element concentrations in bird tissues from Sequoyah with those found in the above mentioned studies yielded no evidence for element contamination at Sequoyah. Thus, available data for sediment, fish, and birds seem to be in general agreement: Sequoyah appears to be a relatively fit environment for fish and wildlife with respect to the elements studied.

## MANAGEMENT CRITERIA AND RECOMMENDATIONS

Organochlorine (OC) compounds were detected at both Sequoyah and Little River, but the magnitude of contamination at the two locations differed greatly. At Little River, no **Oct** were detected in sediment. DDE, which was virtually the only OC found in Little River fish, occurred at low concentrations. Comparison of DDE concentrations in fish from Little River with suggested guidelines for the protection of fish-eating predators, indicated no risk to the latter. The ratio of DDE to other DDT homolog in fish was 1 .0, thus, the source of contamination to the watershed was assumed to be old and well weathered. Conditions at Little River did not appear to warrant further action with respect to **Oct**.

At Sequoyah, the evidence clearly indicates a greater severity of OC contamination. **Oct** were found in some sediment samples. Fish were moderately contaminated, and while the risk to fish-eating birds appeared acceptable, the margin for increased risk was not great. Since the use of OC products has been banned in the United States, the management objective at Sequoyah should be a steady reduction in OC concentrations in the aquatic food-chain. This objective should be documented by monitoring **Oct** in one species of fish, at ten-year intervals, in order to verify the desired trend. It is recommended that beginning in the year 2000, one composite sample of largemouth bass be collected and submitted for OC analysis from each of the following sites on Sequoyah: (1) Negro Creek, (2) Little Vian Creek, (3) Vian Creek, (4) Hezekiah Creek, (5) Dirty Creek, (6) Brier Creek, (7) Sally Jones Lake, (8) Arkansas River backwaters, (9) Illinois River and (10) Canadian River. The resulting data would be compared statistically to data from this study and from each subsequent 10-year collection. Each 10-year interval must be marked by a significant reduction in the mean concentration of each OC compound and by a concurrent increase in the DDE/total DDT ratio. Failure to achieve either of these two criteria would alert resource managers to an appropriate course of action.

No “problem” trace element contamination was evident in the present study at either Sequoyah or Little River, however some form of anthropogenic trace element enrichment is always possible at either location. The management objective at each refuge should be to maintain present baseline concentrations, particularly with respect to those elements known to be potentially toxic.

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